

# Influence of Compost Addition to Soil on the Behaviour of Herbicides

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**Abstract:** The transformations of eight herbicides (atrazine, simazine, terbutryn, pendimethalin, carbetamide, 2,4-D, metsulfuron-methyl and dimefuron) in soil after compost addition were monitored during long-term laboratory incubations. The herbicides were applied to soil, compost and soil-compost mixtures. Herbicide sorption, their kinetics of mineralisation and the extractability of residues were compared in the different treatments. Compost addition to soil generally decreased herbicide mineralisation and favoured the stabilisation of herbicide residues. A fraction of the stabilised residues remained extractable and potentially available. However, most of them were unextractable and formed bound residues. Sorption could be at the origin of a kinetically limited biodegradation, mainly for the most highly-sorbed herbicides (atrazine, simazine, terbutryn, pendimethalin and dimefuron). Compost addition had little effects on the less sorbed herbicides (carbetamide, 2,4-D and metsulfuron-methyl).

**Key words:** sorption, mineralisation, atrazine, simazine, terbutryn, pendimethalin, carbetamide, 2,4-D, metsulfuron-methyl, dimefuron

## 1 INTRODUCTION

Composting is a developing alternative for municipal solid waste management which should develop in the near future. It provides an organic amendment useful to improve soil structure and nutrient status, with effects on physical, chemical and biochemical soil properties.<sup>1–4</sup> The addition of organic amendments increases the soil organic matter content and generally stimulates the soil microbial activity. The consequent modification of pesticide behaviour varies with the nature and reactivity of the organic amendments and with their effect on microbial activity.<sup>5,6</sup> The first effect of organic amendment addition to soil is increase of pesticide sorption,<sup>7–9</sup> thus decreasing leaching.<sup>9–11</sup> This may limit pesticide pollution but can reduce pesticide efficiency, mainly for pesticides applied directly to the soil, such as root-absorbed herbicides. On the other hand, some organic amendments produce soluble organic matter which promotes pesticide desorption and enhances their apparent water solubility through stable interactions in solution between pesticide and soluble organic matter.<sup>12,13</sup>

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Pesticide degradation in soils amended with organic materials can also be modified, depending on the organic amendment and the pesticide properties. A reduction in degradation is usually explained by the decrease of pesticide availability after sorption increase.<sup>14</sup> In contrast, an increase in degradation may be explained by soil microbial activation after the organic amendment application, which favours pesticide degradation by co-metabolism.<sup>15</sup>

Several works report pesticide behaviour during the composting of different organic materials, and the use of composting as a bioremediation technique for contaminated soils<sup>2,16</sup> but few works describe the effect of compost addition on the behaviour of pesticides in soils.<sup>5</sup>

The present experiments were established to gain further information on the fate of several herbicides in the presence of a municipal solid waste compost. The herbicides were <sup>14</sup>C-labelled, which allowed measurement of their mineralisation and chromatographic characterisation of the pesticide residues after extraction. The variation of the results with the amount of compost added was studied.

## 2 MATERIALS AND METHODS

### 2.1 Soil and compost

The soil (*typic Eutrochrept*) was sampled in the surface layer (0–20 cm) of a bare experimental plot located at Grignon (France). It had pH 7.3 with 22% clay, 73% silt, 1.08% organic C and 0.13% organic N (percentages expressed on a dry weight basis).

The compost was formed from the organic fraction of the municipal solid household wastes of Bapaume (France). The windrow fermentation lasted six weeks and was followed by seven months of maturation. The compost pH was 8.5 and organic C and N represented 16.87 and 1.34% of dry compost respectively.

### 2.2 Herbicides

Eight herbicides were used: atrazine, simazine, terbutryn, pendimethalin, carbetamide, 2,4-D, metsulfuron-methyl and dimefuron. All herbicides were uniformly  $^{14}\text{C}$ -labelled on the aromatic ring, except for metsulfuron-methyl in which the  $^{14}\text{C}$  was in the C2 position of the triazine ring. Atrazine was purchased from Amersham (Les Ulis, France) and 2,4-D from Sigma (St Quentin, France). Simazine and terbutryn were supplied by Ciba-Geigy (Basel, Switzerland), pendimethalin by Cyanamid (Princeton, NJ, USA), carbetamide and dimefuron by Rhone-Poulenc Agrochimie (Lyon, France). Metsulfuron was synthesised by Dr J. Bastide (GERAP, Perpignan, France). All the labelled molecules had a radiopurity higher than 97%. Their specific activities are presented in Table 1. Samples of unlabelled chemicals were obtained from the same sources, except for atrazine and 2,4-D which were purchased from ChemService (West Chester, PA, USA).

### 2.3 Sorption experiments

Solutions of  $^{14}\text{C}$ -herbicides were prepared in calcium chloride solution (0.01 M). Ten millilitres of these solutions were added to 5 g of air-dried soil or 1 g of air-dried compost, both 2 mm-sieved into 25-ml Corex centrifuge tubes with Teflon caps. Duplicate samples were established with herbicides at initial concentrations within the range of 0.9 to 1.1 mg litre $^{-1}$ , except for pendimethalin and simazine where the initial concentrations were respectively 0.36 and 0.18 mg litre $^{-1}$ . The radioactivity of the herbicide solutions ranged between 350 and 800 kBq litre $^{-1}$ , except for the metsulfuron-methyl solution where the radioactivity was 103 kBq litre $^{-1}$ . After shaking for 24 h, the samples were centrifuged at 5000g for 15 min and the herbicide concentrations in solution were calculated from the supernatant radioactivity measurements with a liquid scintillation counter (Kontron Betamatic V; Kontron Ins., Montigny le Bretonneux, France). The herbicide sorption ( $S$  in mg kg $^{-1}$ ) was calculated from the difference of herbicide concentration before and after sorption. The sorption coefficient  $K_d$  (litre kg $^{-1}$ ) was calculated as [ $K_d = S \text{ Ce}^{-1}$ ], where  $\text{Ce}$  (in mg litre $^{-1}$ ) was the concentration of the equilibrium solution after sorption. The sorption coefficient on an organic carbon unit basis,  $K_{oc}$ , was calculated as [ $K_{oc} = 100 K_d \text{ C}^{-1}$ ] with  $\text{C}$ , the soil organic carbon content (%).

### 2.4 Incubation experiments

Degradation of the herbicides was followed during laboratory incubations of eight months, in the dark at 28( $\pm 1$ )°C in sealed 500-ml jars, with fresh soil (50 g) and soil-compost mixtures containing 10, 20 and 30% (weight/weight) of compost. Incubations with compost only were also set up. Here, 25 g of inert sand was added to 25 g of compost. The herbicide solutions were

TABLE 1  
Specific Activities of Radiolabelled Herbicides and Amounts Applied during the Incubation Experiments

Herbicide	Water solubility <sup>a</sup> (mg litre $^{-1}$ )	Specific activity (MBq mmol $^{-1}$ )	Amount applied during incubation experiments	
			(kBq kg $^{-1}$ )	(mg kg $^{-1}$ )
Pendimethalin	0.3	267	104	0.12
Simazine	5	200	191	0.18
Dimefuron	16	1147	87	0.33
Terbutryn	25	239	303	0.39
Atrazine	33	659	153	0.34
2,4-D	620	744	88	0.49
Metsulfuron-methyl	1100	137	25	0.35
Carbetamide	3500	999	103	0.37

<sup>a</sup> Data from Ref. 38.

used to adjust the water content of the soil, compost and soil–compost mixtures to 95% of their water-holding capacity. Thereafter, the water content was adjusted monthly by weighing. The incubations were set up in triplicate. The amounts of herbicide and radioactivity applied are given in Table 1. The [ $^{14}\text{C}$ ] carbon dioxide evolved was trapped in sodium hydroxide solution (0.5 M, 10 ml) and periodically measured by scintillation counting.

## 2.5 Herbicide analysis

At the end of the incubations, each sample of soil, compost and soil–compost mixtures was extracted during 24 h with methanol ( $3 \times 100$  ml) by an end-over-end shaking. The extracted radioactivity was directly measured in the methanol extracts by scintillation counting. The non-extractable radioactivity, corresponding to the 'bound residues', was measured by scintillation counting of the [ $^{14}\text{C}$ ] carbon dioxide evolved after combustion of the solid residues after methanol extraction (Sample Oxidizer 307, Packard, Meriden, CT, USA). The three methanol extracts were pooled for each sample and then concentrated until dryness by evaporation with a TurboVap II Concentrator (Zymark, Hopkinton, MA, USA) at 45°C on an helical flow of air with an operating pressure of 800 kPa. The residue was then dissolved in the solvent used for the HPLC analysis of each herbicide (2 ml), filtered through a Cameo 13N syringe nylon filter (0.45  $\mu\text{m}$ ; MSI, Westboro, MA, USA). All samples were analysed using a Waters HPLC appliance (600E Multi-solvent Delivery System, 717 Autosampler and a Novapak C18 column of 5  $\mu\text{m}$  and  $150 \times 4.6$  mm;

Waters-Millipore, Milford, MA, USA) equipped with a radioactive flow detector (Packard-Radiomatic Flo-one A550). The chromatographic conditions for each herbicide are summarized in Table 2.

## 3 RESULTS AND DISCUSSION

### 3.1 Herbicides sorption on soil and compost

Most of the studied herbicides were neutral molecules, apart from 2,4-D and metsulfuron. 2,4-D is a carboxylic acid with a pKa of 2.7 and would have been totally dissociated in the experimental conditions as the pH values of the soil and the soil–compost mixtures were higher than 7. Metsulfuron-methyl has a sulfonylurea function which can be deprotonated with a pKa value between 3.3 and 5.2.<sup>17</sup> In contrast, the triazines are weak bases. The pKa of terbutryn in solution is 4.4, and protonated species could exist mainly near the charged surfaces of the organic or mineral sorbents. However, the Cl-triazines (simazine and atrazine) have pKa values lower than 2, and under the experimental conditions used here they can be considered as neutral molecules.

Sorption measurements allow the evaluation of herbicide availability in relation to their capacity to remain in the soil solution. The  $K_d$  and  $K_{oc}$  coefficients for herbicide sorption on soil and compost are presented in Table 3. A gradation was observed in the sorption of herbicides. Metsulfuron-methyl was the least sorbed herbicide, and pendimethalin the most. Low sorption was related to the anionic properties of the molecules (metsulfuron-methyl and 2,4-D) or their high water solubility (carbetamide). Herbicide sorption on compost was characterised by  $K_d$  values 10- to 20-fold higher

TABLE 2  
Chromatographic Conditions for the Eight Herbicides during HPLC Analysis of the Methanol Extracts<sup>a</sup>

Herbicide	Proportions by volume		
	Solvent A	Solvent B	Gradient
Pendimethalin	20/80 : Methanol/water	90/10 : Methanol/water	100%A (15 min) 100%B
Simazine	20/80 : Methanol/water	80/20 : Methanol/water	100%A (15 min) 70%A
Dimefuron	0.05 M AA, <sup>b</sup> pH = 7.4	0.05 M AA, pH = 7.4	(25 min) 100%B
Terbutryn	50/50 : Methanol/water	90/10 : Methanol/water	100%A (20 min) 100%B
Atrazine	20/80 : Methanol/water	80/20 : Methanol/water	100%A (15 min) 70%A
2,4-D	0.05 M AA, pH = 7.4	0.05 M AA, pH = 7.4	(25 min) 100%B
Metsulfuron-methyl	20/80 : Methanol/water	90/10 : Methanol/water	100%A (35 min) 100%B
Carbetamide	+ 0.01 M TBA <sup>c</sup>	+ 0.01 M TBA	
	20/80 : Methanol/water	90/10 : Methanol/water	100%A (35 min) 100%B
	+ 0.01 M TBA	+ 0.01 M TBA	
	20/80 : Methanol/water	90/10 : Methanol/water	100%A (15 min) 100%B

<sup>a</sup> Waters NovaPak C18–4.6  $\times$  150 mm column, flow 0.7 ml min<sup>-1</sup>, injected volume 500  $\mu\text{l}$ .

<sup>b</sup> Ammonium acetate.

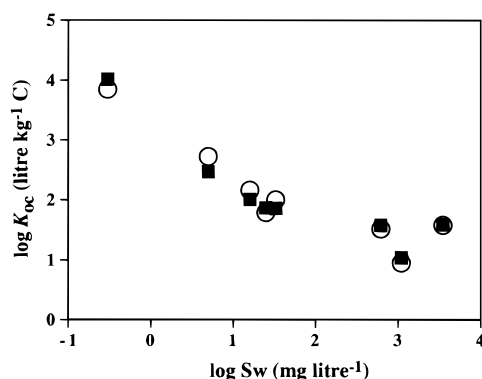
<sup>c</sup> Tetrabutylammonium chloride.

**TABLE 3**  
Partition Coefficients  $K_d$  and  $K_{oc}$  for Herbicide Sorption on Soil and Compost

Herbicide	Soil $K_d$ (litre $kg^{-1}$ )	Compost $K_d$ (litre $kg^{-1}$ )	Soil $K_{oc}$ (litre $kg^{-1}$ C)	Compost $K_{oc}$ (litre $kg^{-1}$ C)
Pendimethalin	110 ( $\pm 6$ )	1194 ( $\pm 30$ )	10 390 ( $\pm 580$ )	7080 ( $\pm 180$ )
Simazine	0.78 ( $\pm 0.01$ )	10.5 ( $\pm 0.3$ )	74 ( $\pm 1$ )	62 ( $\pm 2$ )
Dimefuron	1.08 ( $\pm 0.04$ )	24.6 ( $\pm 0.5$ )	102 ( $\pm 4$ )	146 ( $\pm 3$ )
Terbutryn	3.14 ( $\pm 0.04$ )	89.4 ( $\pm 1.9$ )	296 ( $\pm 4$ )	530 ( $\pm 11$ )
Atrazine	0.76 ( $\pm 0.02$ )	16.8 ( $\pm 0.6$ )	72 ( $\pm 2$ )	100 ( $\pm 4$ )
2,4-D	0.40 ( $\pm 0.01$ )	5.63 ( $\pm 0.10$ )	38 ( $\pm 1$ )	33 ( $\pm 1$ )
Metsulfuron-methyl	0.12 ( $\pm 0.01$ )	1.46 ( $\pm 0.12$ )	11 ( $\pm 1$ )	9 ( $\pm 1$ )
Carbetamide	0.41 ( $\pm 0.01$ )	6.45 ( $\pm 0.08$ )	39 ( $\pm 1$ )	38 ( $\pm 1$ )

than on soil, which was related to the higher organic matter content of the compost.

The  $K_{oc}$  coefficient represents the sorption on a unit C basis and allows a comparison of sorption on compounds with different organic matter content.<sup>18</sup> The  $K_{oc}$  coefficients were inversely related to the herbicide solubility in water (Fig. 1), which is generally observed for most of the neutral chemicals.<sup>19,20</sup> The differences between  $K_{oc}$  measured in soil and compost (Table 3)

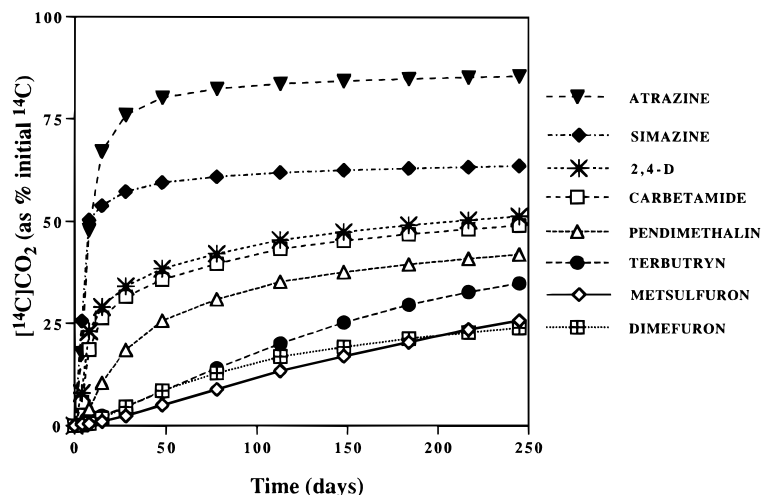


**Fig. 1.** Relationship between herbicide water solubility ( $S_w$ ) and sorption coefficient ( $K_{oc}$ ) in (■) soil and (○) compost.

could be an indication of the different interactions involved in sorption, and related to the organic constituent characteristics. The differences were negligible for the most water-soluble herbicides (carbetamide, metsulfuron-methyl and 2,4-D), which had  $K_{oc}$  values lower than 50 litre  $kg^{-1}$  C. On the other hand, the least water-soluble herbicides (simazine and pendimethalin) had higher  $K_{oc}$  values in soil than in compost. The water-solubilities of dimefuron, terbutryn and atrazine were intermediate, between 16 and 30 mg litre<sup>-1</sup>, corresponding to octanol/water partition coefficients ( $K_{ow}$ ) between 300 and 3000. For these three herbicides, the  $K_{oc}$  coefficients were higher in compost than in soil.

### 3.2 Effect of compost addition on the kinetics of herbicides mineralisation

The kinetics of herbicide mineralisation during soil incubation without compost are shown in Fig. 2 and the total mineralised radioactivities at the end of the incubations are in Table 4. The fastest rate of mineralisation was observed for atrazine, 85% of the initially applied radioactivity being mineralised at the end of the incubation. As for atrazine, simazine mineralisation



**Fig. 2.** Kinetics of herbicide mineralisation during incubation in soil only. The confidence intervals of the measurements at the end of the incubations are reported in Table 4; they were smaller than symbol size throughout all the incubations.

**TABLE 4**  
Total Mineralised Radioactivity at the End of Herbicide Incubations, Percentage of Initial  $^{14}\text{C}$

Herbicide	Soil	10% Compost	20% Compost	30% Compost	Compost
Pendimethalin	42.0 ( $\pm 0.9$ )	23.7 ( $\pm 2.8$ )	17.0 ( $\pm 0.5$ )	16.0 ( $\pm 1.3$ )	14.1 ( $\pm 1.7$ )
Simazine	63.6 ( $\pm 1.3$ )	60.1 ( $\pm 1.6$ )	51.8 ( $\pm 2.5$ )	45.1 ( $\pm 2.2$ )	22.7 ( $\pm 0.5$ )
Dimefuron	24.0 ( $\pm 0.7$ )	12.4 ( $\pm 0.6$ )	8.0 ( $\pm 3.0$ )	4.4 ( $\pm 0.6$ )	2.0 ( $\pm 0.4$ )
Terbutryn	34.9 ( $\pm 0.8$ )	11.2 ( $\pm 1.0$ )	6.0 ( $\pm 0.4$ )	4.1 ( $\pm 0.2$ )	1.4 ( $\pm 0.6$ )
Atrazine	85.5 ( $\pm 2.1$ )	66.0 ( $\pm 5.4$ )	46.9 ( $\pm 3.7$ )	34.0 ( $\pm 2.5$ )	9.9 ( $\pm 2.0$ )
2,4-D	51.3 ( $\pm 0.9$ )	47.4 ( $\pm 1.7$ )	43.6 ( $\pm 0.8$ )	41.0 ( $\pm 2.5$ )	40.0 ( $\pm 2.3$ )
Metsulfuron-methyl	25.7 ( $\pm 1.3$ )	23.2 ( $\pm 0.6$ )	16.5 ( $\pm 0.7$ )	14.9 ( $\pm 2.5$ )	11.9 ( $\pm 0.9$ )
Carbetamide	49.1 ( $\pm 1.6$ )	51.6 ( $\pm 1.3$ )	52.3 ( $\pm 1.3$ )	52.3 ( $\pm 1.3$ )	56.1 ( $\pm 2.5$ )

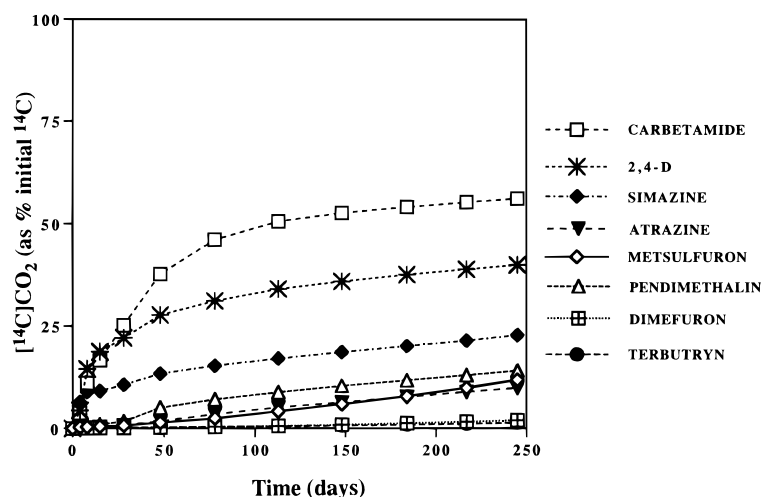
started quickly and reached 64% of the initial radioactivity at the end of the incubation. These results confirmed the previously observed important capacity of mineralisation of the Cl-triazine ring in the soil.<sup>21</sup> For terbutryn, Cl substitution by a methylthio group on the triazine ring modified the shape of the mineralisation kinetics and the mineralisation rate, which reached only 35% of the applied radioactivity at the end of the incubation. The mineralisation kinetics of metsulfuron-methyl,  $^{14}\text{C}$ -labelled on the triazine ring, was similar to that of terbutryn, which confirmed that triazine ring mineralisation was effectively related to Cl substitution.

The lowest rates of herbicide mineralisation during the soil incubation without compost were observed for metsulfuron-methyl, dimefuron, terbutryn and pendimethalin. These rates involved a latency time at the beginning of the incubation, the longest being four weeks for metsulfuron-methyl. Herbicide mineralisation was not directly related to sorption characteristics on soil, as strongly sorbed molecules were mineralised quickly or conversely, weakly sorbed molecules were mineralised slowly. The molecular structure and the localisation of the  $^{14}\text{C}$  labelling in each molecule were of importance also.

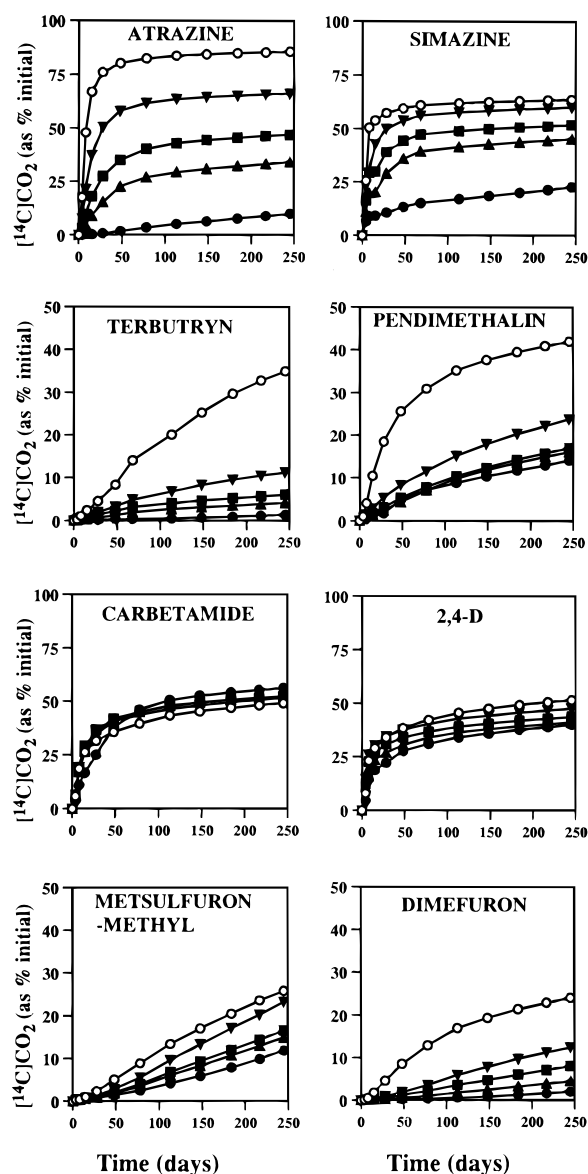
The kinetics of herbicide mineralisation during the compost incubation without soil are presented in Fig. 3 and the total mineralised radioactivities are in Table 4. All the mineralisation rates decreased during the compost incubations compared to the soil incubations, except for carbetamide. The kinetics of atrazine mineralisation involved a latency time of approximately one month during which the  $^{14}\text{C}$  carbon dioxide evolved was negligible, as for metsulfuron-methyl and pendimethalin. The mineralisation of dimefuron and terbutryn was very low and less than 2% of the applied radioactivity was mineralised at the end of the compost incubation.

During incubation of the soil-compost mixtures, herbicide mineralisation decreased as compared to the incubation in soil alone (Fig. 4 and Table 4). The only exception was for carbetamide, where compost addition to soil slightly increased the mineralisation rate. The addition of compost with a high pH increased the soil pH from 7.3 to 7.6–8.3, depending on the proportion of compost. This could have favoured an abiotic hydrolysis as carbetamide hydrolysis occurs at alkaline pH.<sup>22</sup>

For all the herbicides, with the exception of carbetamide, the mineralisation kinetics during incubation of



**Fig. 3.** Kinetics of herbicide mineralisation during incubation in compost only. The confidence intervals of the measurements at the end of the incubations are reported in Table 4; they were smaller than symbol size throughout all the incubations.



**Fig. 4.** Kinetics of herbicide mineralisation during incubation in (○) soil alone, in (▼) 10, (■) 20 and (▲) 30% w/w compost soil mixtures, and (●) compost alone. The confidence intervals of the measurements at the end of the incubations are reported in Table 4; they were smaller than the symbol size throughout all the incubations.

soil–compost mixtures were between those obtained during incubations with soil alone and compost alone. For atrazine, simazine and metsulfuron-methyl mineralisation decreased as the proportion of compost increased. For 2,4-D and carbetamide, compost addition did not influence the mineralisation kinetics, whatever the compost proportion was. For other herbicides (terbutryn, pendimethalin and dimefuron) the smallest proportion of compost was enough to decrease sharply the mineralisation of the molecules. Increasing the compost proportion did not greatly influence the compost effect.

Modification of the mineralisation kinetics after compost addition to soil was related to the sorption

properties of the herbicides on soil and compost. Few alterations were observed for the less-sorbed herbicides, such as the carbetamide and 2,4-D, with  $K_{oc} < 50$  litre  $kg^{-1}$  C. The mineralisation decrease was related to the proportion of compost for atrazine and simazine, which had  $K_{oc}$  values lower than 100. For the herbicides which had  $K_{oc}$  values larger than 100, even a low proportion of compost strongly decreased mineralisation. The decrease of herbicide available for degradation and mineralisation could be related to herbicide diffusion in the soil–compost mixtures. Compost microporosity was characterised by pores smaller than in soil. Compost addition to soil increased the proportion of small pores<sup>23</sup> and herbicide biodegradation could have been kinetically limited by intraparticle diffusion.<sup>24,25</sup>

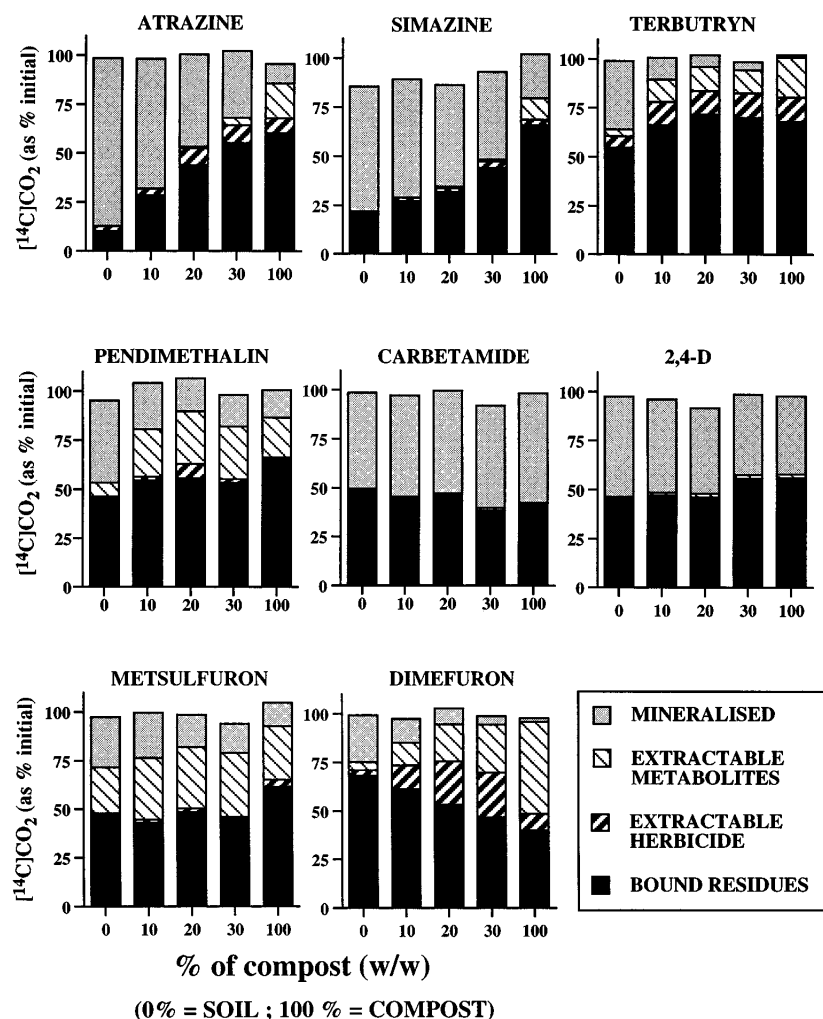
In spite of the low sorption of metsulfuron-methyl, a gradual decrease of the mineralisation was observed when the proportion of compost increased. Thus may be related to the  $^{14}C$ -labelling of the triazine ring. During metsulfuron-methyl degradation, hydrolysis of the sulfonyl group released the triazinic moiety (4-methoxy-6-methyl-1,3,5-triazine-2-amine)<sup>26</sup> which then acted as the other triazines.

### 3.3 Effect of compost addition on the extractability of herbicide residues

Tables 4, 5 and 6 and Fig. 5 present the distribution of radioactivity at the end of the incubation between mineralised, methanol-extractable and non-extractable fractions. HPLC analysis of the methanol extracts indicated some metabolic modifications after compost addition. Figure 6 shows examples of chromatograms of extracts after herbicide incubation in soil, compost and soil–30% compost mixture. The herbicide metabolites were not identified except for those from atrazine. Most of the metabolites were molecules with retention times shorter than those of the corresponding herbicide. However, for pendimethalin, one of the metabolites was characterised by a longer retention time than pendimethalin after incubation in soil with 20 and 30% compost.

Most of the unmineralised residues remained in the soil as bound residues. The formation of bound residues is common for many organic chemicals in soils, and their proportion depends on the herbicide and soil properties.<sup>27–29</sup>

For carbetamide and 2,4-D, the extractable fraction represented less than 2% of the initially applied radioactivity. On the other hand, for carbetamide and 2,4-D, respectively 38–48% and 45–56% of the initial radioactivity was found as bound residues at the end of the incubation (Table 6). For these two herbicides, compost addition did not have a significant influence on bound residue formation. Their degradation in soils is mainly of biological origin with formation of very reactive



**Fig. 5.** Distribution of herbicide radioactivity between mineralised fraction, extractable and non-extractable (bound residues) fractions at the end of herbicide incubations in soil, compost and soil-compost mixtures. In the extractable fraction, the proportion of the untransformed herbicide is indicated. The confidence intervals of the measurements are reported in Tables 4, 5 and 6.

metabolites, 2,4-dichlorophenol for 2,4-D,<sup>6,30</sup> and aniline for carbetamide,<sup>31</sup> which may form bound residues. For these herbicides, slightly sorbed and with simple chemical structures, mineralisation kinetics gave a good indication of their behaviour in soil.

For atrazine and simazine, the proportion of bound residues formed increased with the compost proportion. The proportion of the extractable residues also

increased to a maximum in the incubation of compost without soil. The proportion of atrazine and simazine in the methanol extracts decreased when the proportion of compost increased. In the presence of compost, a partial degradation of atrazine and simazine occurred. However, a fraction of the untransformed herbicides and of their metabolites remained extractable and potentially available.

**TABLE 5**  
Total Extractable Radioactivity in Methanol at the End of Herbicide Incubations, Percentage of Initial <sup>14</sup>C

Herbicide	Soil	10% Compost	20% Compost	30% Compost	Compost
Pendimethalin	7.9 (±0.3)	26.0 (±3.3)	34.0 (±1.2)	28.9 (±2.2)	20.4 (±3.5)
Simazine	1.4 (±0.4)	1.9 (±0.2)	2.7 (±0.3)	4.0 (±1.4)	13.6 (±1.7)
Dimefuron	7.0 (±0.8)	23.8 (±1.5)	41.4 (±3.1)	47.5 (±1.2)	55.8 (±2.7)
Terbutryn	9.4 (±0.8)	23.2 (±0.8)	24.5 (±1.3)	24.3 (±2.3)	32.9 (±1.2)
Atrazine	2.5 (±0.4)	3.5 (±0.9)	9.3 (±0.4)	12.9 (±2.4)	25.4 (±0.6)
2,4-D	1.4 (±0.2)	1.6 (±0.5)	1.9 (±0.3)	1.9 (±0.3)	1.8 (±0.4)
Metsulfuron-methyl	23.8 (±1.3)	33.2 (±5.5)	33.4 (±2.3)	33.1 (±3.9)	31.1 (±2.1)
Carbetamide	1.3 (±0.2)	1.2 (±0.5)	1.1 (±0.2)	1.2 (±0.3)	1.1 (±0.1)

**TABLE 6**  
Total Non-extractable Radioactivity (Bound Residues) at the End of Herbicide Incubations, Percentages of Initial  $^{14}\text{C}$

Herbicide	Soil	10% Compost	20% Compost	30% Compost	Compost
Pendimethalin	45.4 ( $\pm 0.6$ )	54.5 ( $\pm 3.0$ )	55.6 ( $\pm 3.6$ )	53.2 ( $\pm 1.2$ )	66.2 ( $\pm 2.8$ )
Simazine	20.3 ( $\pm 3.3$ )	27.2 ( $\pm 3.1$ )	31.9 ( $\pm 5.8$ )	44.2 ( $\pm 3.3$ )	66.1 ( $\pm 5.0$ )
Dimefuron	68.1 ( $\pm 3.0$ )	61.2 ( $\pm 3.6$ )	53.2 ( $\pm 2.8$ )	46.9 ( $\pm 3.6$ )	40.0 ( $\pm 2.7$ )
Terbutryn	54.6 ( $\pm 1.0$ )	66.3 ( $\pm 7.0$ )	71.7 ( $\pm 5.4$ )	70.1 ( $\pm 7.1$ )	68.1 ( $\pm 6.3$ )
Atrazine	10.4 ( $\pm 0.6$ )	28.6 ( $\pm 3.0$ )	44.1 ( $\pm 2.3$ )	55.3 ( $\pm 3.2$ )	60.4 ( $\pm 5.2$ )
2,4-D	44.9 ( $\pm 0.5$ )	47.0 ( $\pm 2.7$ )	46.0 ( $\pm 3.1$ )	55.6 ( $\pm 5.9$ )	56.0 ( $\pm 2.2$ )
Metsulfuron-methyl	47.8 ( $\pm 0.5$ )	43.1 ( $\pm 4.0$ )	48.6 ( $\pm 2.3$ )	46.0 ( $\pm 1.9$ )	61.7 ( $\pm 2.9$ )
Carbetamide	48.1 ( $\pm 2.2$ )	44.4 ( $\pm 0.9$ )	46.2 ( $\pm 1.4$ )	38.5 ( $\pm 3.2$ )	41.2 ( $\pm 2.6$ )

Three major atrazine metabolites were detected: hydroxy-atrazine at 24 min, deethyl-atrazine at 21 min and deisopropyl-atrazine at 16 min (Fig. 6). The contribution of these metabolites to the extractable radioactivity was important only with compost proportions higher than 30%. During incubation with compost alone, atrazine and deethyl-atrazine each represented 30% of the extracted radioactivity, deisopropyl-atrazine 19% and hydroxy-atrazine 12% of the extracted radioactivity. The modification of pesticide degradation in soil by addition of organic matter depends on the nature of the added organic matter. For instance, the dealkylation of triazines and phenylureas in soils seems to be inhibited by sewage sludge addition, but is favoured by manure addition.<sup>10</sup> The fate of the metabolites varies with their nature. The dealkylated derivatives of atrazine have a higher tendency to form bound residues than has atrazine; on the other hand, hydroxy-atrazine stabilisation occurs mainly through sorption which inhibits the formation of bound residues.<sup>32</sup>

For simazine, only a small proportion of the initial radioactivity remained extractable at the end of the incubation. Some metabolites were identified only in the extracts from incubation with compost alone (Figs 5 and 6). The degradation pathways of simazine and atrazine in soils are similar. The rapid mineralisation of both molecules indicated the presence of specific microflora adapted to triazine ring mineralisation in the soil. The effect of compost addition on the degradation of these herbicides could have been different in a soil where the triazine ring mineralisation is slower.

The behaviour of terbutryn was similar to that of atrazine and simazine. However the effect of compost addition on terbutryn behaviour was important since the lowest proportion used caused significant changes (Fig. 5). At the end of the incubation of terbutryn in soil alone, only 9% of the initial radioactivity was recovered as extractable residues and 55% formed bound residues. When compost was added, the bound residues represented between 66 and 72% of the applied terbutryn (Table 6). The amount of terbutryn in the extractable fraction was equivalent in all the incubations with

compost, representing 12% of the applied terbutryn. As for atrazine and simazine, the proportion of metabolites in the extracted radioactivity after incubation was higher in compost, representing 20% of the applied radioactivity, than in soil or soil-compost mixture. The proportion of terbutryn decreased in the methanol extracts. Simultaneously, the proportions of the metabolites characterised by retention times of 5 and 26.5 min increased. During incubation with compost, another metabolite appeared in the methanol extract with a retention time of 12 to 13 min, which was absent after terbutryn incubation in soil alone or soil-compost mixtures (Fig. 6).

For pendimethalin, the distribution of extractable residues according to the compost proportion followed the same pattern as terbutryn (Fig. 5). However, the proportion of untransformed pendimethalin in the extracts was smaller (Fig. 5). The highest proportion of extracted pendimethalin represented 7% of the applied radioactivity in the incubation with 20% of compost. No pendimethalin was found in the methanol extract after incubation in compost alone and the extracted radioactivity corresponded to polar metabolites chromatographed at a retention time shorter than 8 min (Fig. 6). Pendimethalin and its metabolites are protected against biodegradation through sorption on organic matter.<sup>33-35</sup> Like other dinitroanilines, pendimethalin forms large amounts of bound residues.<sup>36</sup> Compost addition slightly increased the formation of bound residues.

Compost addition to soil did not modify the distribution of residues of metsulfuron-methyl (Fig. 5). A large part of the residues remained extractable, 24% after soil incubation and 33% after incubation of the different soil-compost mixtures. Only traces of metsulfuron-methyl were detected in the methanol extracts, except in the incubation with compost alone, in which the extracted metsulfuron-methyl represented 3% of the initially applied amount. The monitoring of the metsulfuron behaviour strongly depended on the localisation of the  $^{14}\text{C}$  in the triazine moiety. The chromatograms of the methanol extracts showed that almost no extracted



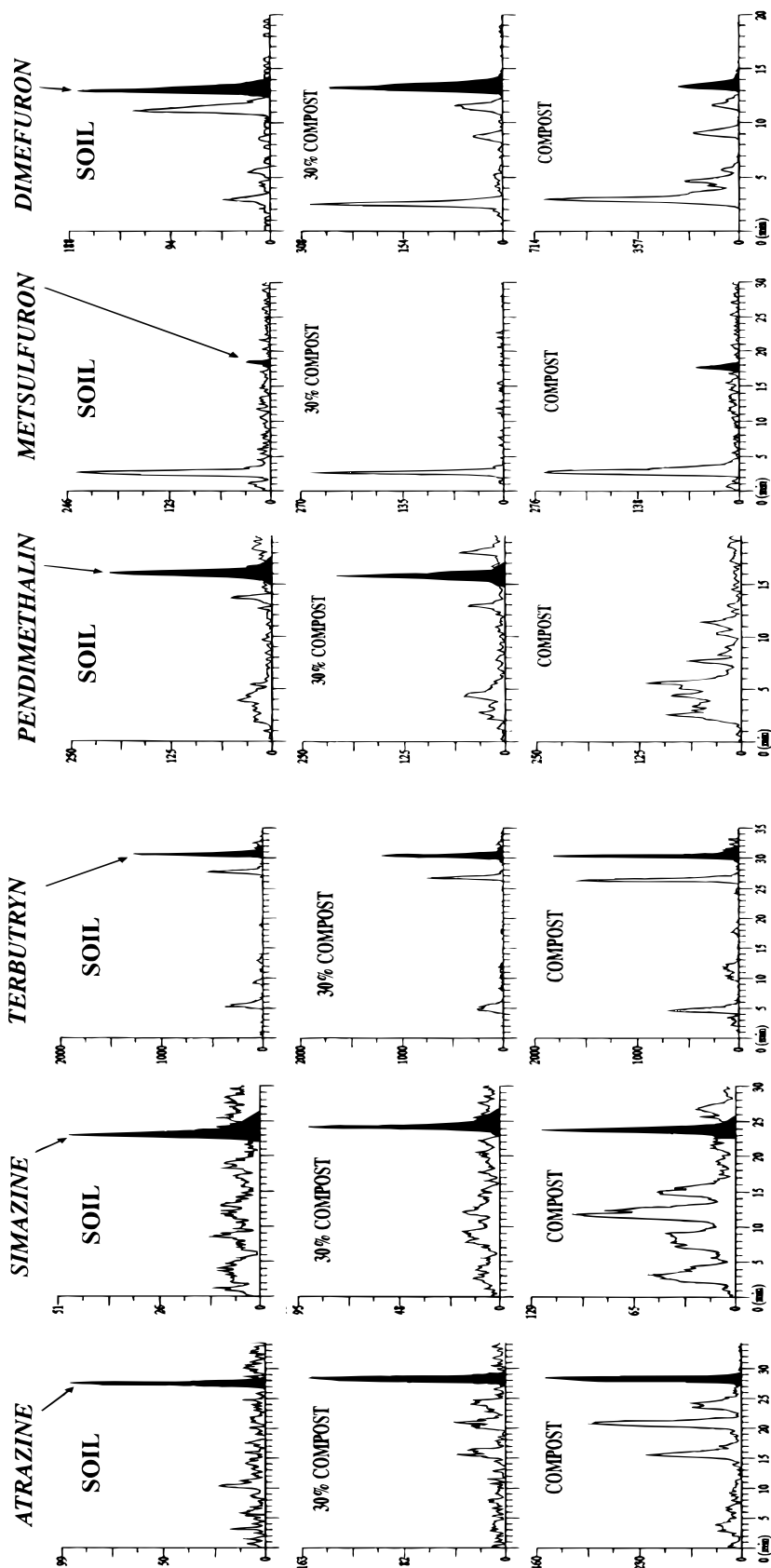


Fig. 6. Examples of chromatograms with  $^{14}\text{C}$  detection of herbicide residues extracted at the end of incubation in soil, compost and soil with 30% compost.

radioactivity was retained under chromatographic conditions used, which gave indications about the high polarity of the extracted metabolites (Fig. 6). The most frequent metabolite of metsulfuron-methyl in soils is 4-methoxy-6-methyl-1,3,5-triazine-2-amine, which is very polar. In field experiments, this metabolite represented 50 to 85% of the radioactivity remaining in the soil after six months.<sup>37</sup> Another unidentified polar metabolite has been found in similar proportion to 4-methoxy-6-methyl-1,3,5-triazine-2-amine during soil incubation in non-sterile conditions, but was absent in sterile conditions.<sup>26</sup>

The distribution of the dimefuron residues after incubation was different from that of the other herbicides (Tables 5 and 6, Fig. 5). Compost addition decreased the mineralisation of dimefuron, as for the other herbicides. However, in the case of dimefuron, the decrease in mineralisation was associated with a decrease in the formation of bound residues. The proportion of extractable radioactivity increased with the proportion of compost in the soil-compost mixtures to a maximum with compost alone. On the other hand, the proportion of extractable dimefuron increased with the proportion of compost in the soil-compost mixtures up to 22% of the applied radioactivity with 20% of compost. However, compost addition favoured the degradation of dimefuron and allowed the metabolites formed to remain extractable. The largest proportion of metabolites was measured during incubation with compost alone, and represented 47% of the applied radioactivity. These results could correspond to a specific dimefuron degradation by the compost microflora with the release of less-degradable metabolites or protected against degradation by the presence of the compost. These metabolites had a lower tendency to form bound residues than dimefuron. The release of very polar metabolites was observed when compost was added (Fig. 6). These polar metabolites and those chromatographed at 9 min seemed to characterise the incubation in presence of compost. On the other hand, the metabolite at 11.5 min seemed mainly associated to the soil.

#### 4 CONCLUSIONS

In this work, all the herbicides studied formed a high proportion of bound residues. It was often higher than 40% of the applied radioactivity, and represented 50 to 100% of the unmineralised residues at the end of the incubations. The bound residues could be considered as the result of a stabilisation process, because their degradation or mineralisation rates are considerably decreased as compared to those of the corresponding herbicides. Different hypotheses are proposed to explain bound residues formation, including chemical binding to soil organic compounds, trapping in the internal voids of soil organic matter, incorporation into phenolic

polymers and bioincorporation in cellular structures through the activity of soil micro-organisms.<sup>27,29</sup>

Compost addition increased the soil organic matter and could partly explain the increase of the stabilisation of herbicide residues. This was mainly true for the most highly-sorbed herbicides and could indicate that stabilisation occurred mainly through sorption processes. However, it was not possible to dissociate the effects of the organic matter increase and the modification of the microbial activity after compost addition. The kinetics of [<sup>14</sup>C] carbon dioxide release gave an indication of the capacity of the microflora to use the herbicide or its metabolites as metabolic substrates. For the three triazines (atrazine, simazine and terbutryn) at the end of the incubation, the proportion of the remaining radioactivity present as extractable residues decreased with the proportion of mineralised radioactivity. Simultaneously the proportion of the remaining radioactivity present as bound residues increased. This could indicate that bound residue formation was related to biological activity and to biotransformation of the herbicides. The specific behaviour of dimefuron confirmed this hypothesis. For this herbicide, compost addition decreased the mineralisation and the formation of bound residues, most of the residues remaining extractable.

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